

CONF 771024-1

TITLE: ENVIRONMENTAL POLLUTION BY TRACE ELEMENTS IN COAL PREPARATION WASTE

AUTHOR(S): J. M. Williams, E. M. Wewerka, N. E. Vanderborgh,
P. Wagner, P. L. Wanek and J. D. Olsen

SUBMITTED TO: 7th Symposium on Mine Drainage Control, at
NCA/BCR Coal Conference, Louisville, KY, Oct. 19, 1977

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

By acceptance of this article for publication, the publisher recognizes the Government's (license) rights in any copyright and the Government and its authorized representatives have unrestricted right to reproduce in whole or in part said article under any copyright secured by the publisher.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the USERDA.


los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

MAS

IN COAL PREPARATION WASTES*

J. M. Williams, E. M. Wewerka, N. E. Vanderborgh,
P. Wagner, P. L. Wanek and J. D. Olsen

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

INTRODUCTION

Coal is gaining new strength as the world searches for more energy. Coal is not a very clean fuel, however. Many of its problems can be traced back to its basic composition, i.e., a sedimentary formation of combustible, organic material containing inorganic rock and mineral matter. When mined, additional inorganic material which surrounds the coal seam may be taken as coal seams are stripped as rapidly and as economically as possible. From an environmental viewpoint, the mineral matter in coal produces undesirable gaseous and particulate pollutants which escape into the atmosphere when the coal is burned. To reduce these problems, about one-half of all the coal mined in the U. S. is cleaned or prepared near the mine to remove some of the heavier, unwanted, mineral matter from the lighter coal.¹ The prepared coal that is sent to the power plant is cleaner and thus produces less air contamination when burned than if it were not cleaned. The coal preparation waste left behind, however, is not always innocuous. The choice appears to be between possible terrestrial pollution from coal preparation wastes and obvious atmospheric pollution if these same materials were burned in the coal.

Coal preparation wastes contain a broad array of accessory or trace elements.² Some elements, such as iron, sulfur, aluminum, silicon, potassium, calcium, magnesium, titanium and sodium are present near or above the one percent level.² These elements form the major mineral species, such as pyrite, clays, quartz, calcite, and rutile. Almost all the other elements are present in much lesser amounts.² The chemistry of the various trace elements in the coal waste structure is less well understood than it is in coal itself where, for all the years of study, the subject of minor and trace element chemistry and associations is still debated. In any waste pile, however, each element will have some propensity to be leached and thereby carried into the aquatic environment. Investigators in several laboratories throughout the country are working at trying to understand how the elements are associated in coal and coal wastes, and thereby what their leaching propensity might be, but, until this is accomplished, the most enlightening information about element levels in waste-pile drainages appears to be the drainages themselves.

Trace or accessory elements are beginning to be recognized as serious water-borne contaminants. The concern about elements in coal waste drainage stems from the sensitivity of plant and animal life to them. All elements can be tolerated at some level, but many cause mortality at even very low levels. For example, it has been reported that as little as 400 ppm of Fe or Al ions in soils can result in the mortality of plants, and that fish kills may be caused by concentrations of these ions as low as 0.5 ppm.^{3,4} In acid environments, such as exist in the drainages from coal waste piles, it is not unreasonable to expect the levels of some elements to become this high or higher and thus threaten animal and plant life.

Data on element leaching from coal waste are found to be somewhat restricted.² Generally, less than a dozen elements have been studied. Almost all are considered major elements. Other than the acidity-producing ability (measured by leachate acidity and pH) of coal waste, few parameters have been studied which can help predict the behavior of elements in the environment. Not even the percentages of elements that can be leached appear to be known. In short, the environmental

* Work performed under the auspices of the United States Energy Research and Development Administration and Environmental Protection Agency.

Please type to both lines

and

Do not type in this area

behavior of the elements in coal waste piles is very poorly understood.

Through 1975, only a few authors had studied the levels of elements found in the drainage from coal waste piles.² Typically these elements have been those readily measured with atomic absorption, namely Fe, Al, Mn, Ca and Mg. Additional ions less frequently reported, but measured by this technique are Na, K, Zn, Ni and Cu. Very scant quantitative data are available for P, B, Mo, Cl and Pb. Other parameters frequently determined for refuse drainage are pH, sulfate ion and total solids, while total acidity and conductivity are less often measured.

The little quantitative data available support what those who have seen the run-off from coal waste piles would have guessed: the aqueous drainage from coal refuse usually contains considerable dissolved mineral or inorganic matter. For drainages from coal waste piles in Pennsylvania, West Virginia, Kentucky, Indiana and Illinois where the pH was below 3, dissolved iron levels are almost always well above 500 ppm and sulfate ions above 1500 ppm.⁵ Some Pennsylvania coal waste effluents have been found to have greater than 4% sulfate ion, while some Illinois drainages have over 1% dissolved iron.⁵ The highest ion concentrations are generally found in the most acidic drainages.^{3 5} Certainly these elemental ion levels are cause for concern, considering the sensitivity of plant and animal life to many of them.

Recognizing the need to understand the chemistry of environmentally harmful trace elements released in the drainage of coal preparation wastes and the need to develop control technology for removing or recovering the elements of environmental or economic interest, EPA and ERDA, through an interagency agreement, initiated a program at Los Alamos Scientific Laboratory in 1975 to study these problems. The data reported in the technical sections of this paper were obtained as part of that project.

MATERIAL COMPOSITION

The coal preparation waste that we have studied came from the southern part of the Illinois Basin. This basin, which includes Illinois, Indiana, and western Kentucky, is one of the major coal mining areas of the U. S. The coal in this area is highly mineralized, especially with pyrite, which is quite sensitive to oxidation and yields sulfuric acid and soluble iron. The waste material studied is representative of the average daily production of waste produced by a coal preparation plant which cleans over 10,000 tons of coal per day. The mineral content is given in Table I.

The mineral composition of the waste studied fits well into the range typically found in the Illinois Basin.⁶ (Some values like pyrite and marcasite and gypsum may be a little high when the major element content below is considered.) Silica (19%) and aluminosilicates (39%) are the dominant minerals, while pyrite (17%) and surprisingly marcasite (12%) comprise a major portion of the remainder. Residual coal comprises most of the unaccountable material (11%). This sample did have a surprisingly low calcite value. This could lower the inherent acid neutralizing ability of the waste material. Other than this, this material should leach like much of the other coal preparation wastes from this region.

The major elements in the coal waste studied are those which make up the minerals discussed above. A listing is given in Table II. Some trace elements which are potentially hazardous are given in Table III. All these elements are typical of the values found in this area of the Illinois Basin.⁶

..... This is your last page of the report

PLATE I

and

TABLE I

TABLE I	
MINERAL CONTENT OF AN ILLINOIS-BASIN COAL PREPARATION WASTE	
Mineral	Wt. %
Illite	11.7
Kaolinite	7.8
Other Clays	19.5
Quartz	19.2
Pyrite	17.2
Marcasite	12.4
Gypsum	1.2
Calcite	0.0

TABLE II	
MAJOR INORGANIC ELEMENTS IN AN ILLINOIS-BASIN COAL PREPARATION WASTE	
Element	Wt. %
Si	13.6
Fe	11.0
Al	5.1
K	1.1
Ti	0.35
Mg	0.23
Na	0.16
Ca	0.09

TABLE III	
SOME TRACE ELEMENTS IN AN ILLINOIS-BASIN COAL PREPARATION WASTE	
Element	PPM
Mn	147
Zn	124
As	94
V	86
Cr	77
Ni	71
Cu	51
Pb	34
Co	30
Be	2.8
Cd	0.7

STATIC LEACHING STUDIES

Static leaching techniques offer a rapid method for determining the effects of experimental parameters. However, these techniques only roughly approximate the actual environmental conditions encountered. We have used this technique to study time, temperature, particle size, oxygen and pH effects on the element leaching from coal waste materials. A few examples are presented below.

Crushed (-3/8") or powdered (-20 mesh) waste (50 g) was added to 250 ml of leachate (distilled water or dilute sulfuric acid) contained in a 500-ml erlenmeyer flask. The flask was either stoppered or fitted with a modified stopper designed to allow air into the flask while retaining the contents. Heating, when desired, was provided by a variac-controlled heating mantle. The completed flask assembly was inserted into a shaking apparatus that was used to agitate the sample during the experiment. After the completion of the leach period, the sample was removed from the shaker, and the leachate and residue were separated by vacuum filtration. The residue was rinsed with distilled water and the filtrate added to the leachate.

The leachate was tested for pH and then acidified with 6N nitric acid (to prevent precipitate formation) and made up to 250 ml. Aliquots from this were used to determine total solids and elemental ion concentrations.

Selected results for a series of experiments covering waste size and oxygen presence for times up to 8 weeks are given in Figure 1. Illinois-Basin coal waste produces an immediate drop in pH, reaching a value of 2.5 within a contact time of just 10 minutes (Figure 1A). This value continues to drop steadily in the presence of air and is still dropping when it reaches 1.8 in 50 days. In the absence of air, pH rises. (The initial pH drop probably reflects the presence of oxygen in the unpurged, but stoppered flasks.) Presumably, the chemical system is equilibrating through reactions which consume or tie up hydrogen ions. The depletion of

Please type to borderline

and

Do not type in this area

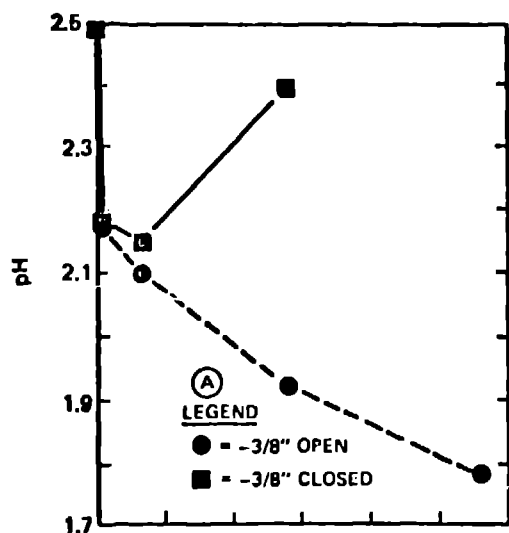
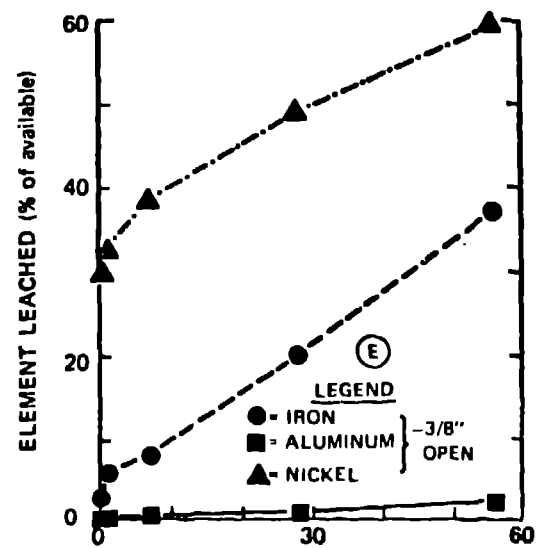
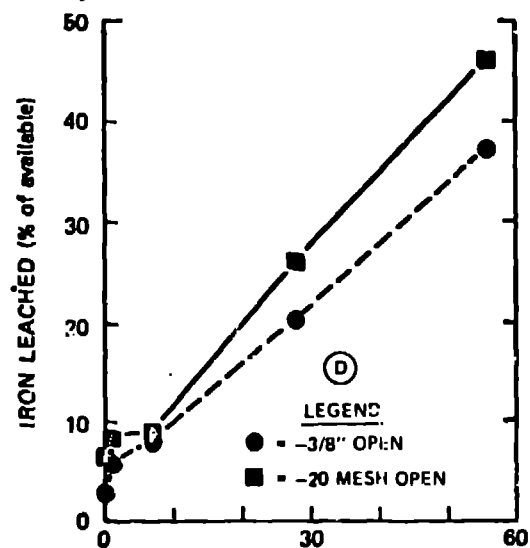
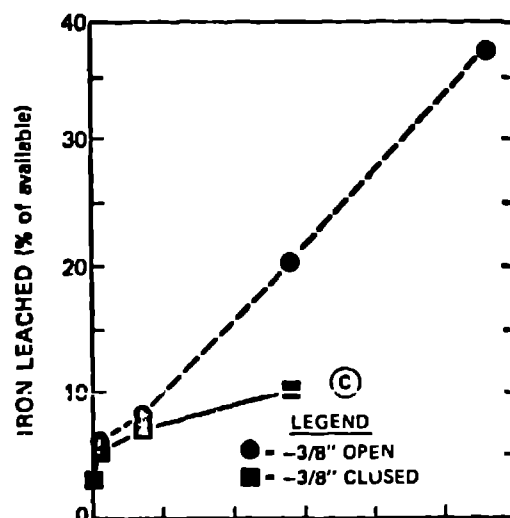
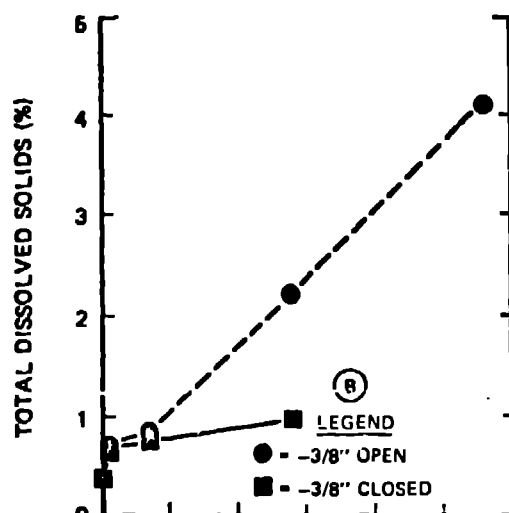


Figure 1. Selected Data from the Static Leaching of an Illinois-Basin Coal Waste Material at Room Temperature.



LEACH TIME (days)

... demonstrated by the formation of a vacuum in the stoppered flasks.

The total dissolved solids in the leachate increases dramatically as the coal waste is shaken in air (Figure 1B). The data here are for a 5-to-1 water-waste ratio and reflect that after 50 days the leachate contains 4% dissolved solids and is increasing approximately 0.07% every day. In the absence of air only minor increases occur.

Very similar results to those for the dissolved solids are observed for iron, which reiterates the sensitivity of this element to oxygen (Figure 1C). The strong leaching power of highly contaminated and acidic leachate with dissolved air is readily apparent when it is seen that 40% of all the iron available is leached from the coal waste in 60 days.

Particle size is also important in coal waste leaching. This is reflected by the nearly 20% increase in iron leached from -20 mesh waste over that from -3/8" waste (Figure 1D). With the trend towards the processing of finer material through the preparation plant (80% of the waste in this plant was minus 2 inches), waste pile leaching will become more severe.

Not all elements behave like iron, which starts out at a relatively low level of solubility and rapidly increases with time (Figure 1E). Aluminum, a major constituent of clays and feldspars, is and remains quite insoluble. Nickel, an element whose mineral association is not known, on the other hand, is much more soluble than iron. Indeed, a wide range of element solubilities might be expected.

An experiment to determine the solubility of a variety of elements in coal waste was conducted on -20 mesh waste under room temperature, open air conditions. Not entirely surprising, the elements which were present in the highest concentrations in the leachate were generally those that were also present in the greatest amount in the bulk material (compare the "amount leached" data in Table IV with the data in Tables II and III). When the percentage of material present in the bulk material that is leached is considered, a very different picture takes shape.

Calcium occurs in a very soluble form in this Illinois-Basin coal waste (see the "% leached" data in Table IV). This is consistent with the presence of gypsum. Cobalt, nickel, zinc, cadmium, and manganese also occur in relatively soluble forms. Frequently thought to occur as sulfides, they do not appear to be related to the bulk of the iron which occurs as pyrite and marcasite and is less soluble. The similarity of vanadium and chromium to the clay elements, aluminum and potassium, suggests that these elements may substitute for aluminum in the clay structure. Titanium is quite insoluble, as would be expected if it occurred as titanium dioxide. This particular compound has been observed in the waste, using an electron microprobe. More conclusive elemental leaching behavior and mineral associations will arise as more data become available. Static leaching experiments will provide a rapid method for providing much of that data.

COLUMN LEACHING STUDIES

Dynamic column leaching experiments provide a laboratory technique to answer a major criticism of the static leaching methods, i.e., they more nearly approximate real-life conditions. On the other hand, dynamic experiments are somewhat more difficult to control, are time consuming, and rarely provide time-dependent, percentage-of-element-leached type data without resorting to mathematical gymnastics. In spite of these difficulties, column leaching experiments provide quite useful information which can be of use to understand how waste piles behave under leaching conditions and to indicate the types of methods that might be necessary to control waste pile leaching.

Crushed waste samples (1500 g) were mixed and carefully loaded (to insure uniform distribution) into a glass column 70 cm long and 4.6 cm in diameter. This

Please type to left of line

and

Do not type in this area

This is your TABLE IV typewritten line
ELEMENTS RELEASED FROM AN ILLINOIS-BASIN COAL WASTE
DURING 4 DAYS OF AQUEOUS LEACHING^(a)

<u>Element</u>	<u>Amount Leached (µg/g of Waste) (b)</u>	<u>Element</u>	<u>% of Total Element Leached</u>
Fe	16400	Ca	79
Ca	680	Co	60
Al	570	Ni	46
Mg	216	Zn	42
<div style="display: flex; align-items: center;"> ← Figures and figure captions within this space - 5 1/4 x 7" → </div>		Cd	35
Na	74	Mn	28
Zn	48	Fe	14
Mn	40	As	9
Ni	31	Mg	9
Co	18	Cu	7
As	7	Be	6
Cu	4	Na	5
Ti	<2	V	<3
V	<2	Cr	1
Cr	1	Al	1
Be	0.2	Pb	<1
Cd	0.2	K	0.8
Pb	<0.2	Tl	<0.1

(a) -20 mesh waste opened to air at room temperature

(b) Also aqueous level if 1 g of waste is leached with 1 g of water

column had previously been drawn at the bottom to provide a small (7 cm) orifice. An overflow tube (7 cm) was provided at the top. Particle retention was insured by placing 5 cm of glass wool at the top and bottom of the column. Distilled water, which had been equilibrated with air and had a 100 cm pressure head was metered upwards through the column to prevent plugging. Flow rates were generally around 45 ml/hr. During experiments where air was passed through the column, the leachate was removed through the bottom orifice and air blown (280 l/hr) upwards.

Leachate samples (35 ml or 100 ml) were collected periodically, their pH determined, and then acidified with 10 volume percent of 6N nitric acid. These acidified samples were then analyzed for total dissolved solids and inorganic elements and the data corrected for dilution.

This is your typewritten line

end

Do not type in this area

continuously through a coal waste column are shown in Figure 2. (A much more comprehensive compilation will appear in the annual report of this project.) The low initial pH value (1.7) is much like the value observed in the static experiments above. The shape of the pH-volume curve reminds one of a weak-acid titration curve. Here the inflection point occurs around 3000 ml or nearly 6 times the volume of water (500 ml) needed to cover the coal waste. The early rise in pH suggests that a moderate amount of acidic material is originally present and that more is not readily formed with the influx of fresh water.

The initial iron content (over 10000 ppm) in leachate from coal waste is high (Figure 2). The level falls off extremely fast and is only a few hundred ppm after 3 liters has passed through the 1500 g mass. The level eventually drops to 10-25 ppm and remains constant after 10 liters have been collected. It would appear that only a certain amount of soluble iron is initially present, that this is flushed out, and that additional soluble iron does not form rapidly.

The iron behavior in the continuous flow system is dramatically different from that in the static system. (Compare the $-3/8$ " open system data in Figure 1C with that in Figure 2, using 1 liter of volume as being approximately equal to 1 day of time.) The failure of significant amounts of soluble iron to form in the flowing system suggests the absence of the proper conditions in this system to oxidize pyrite. The importance of oxygen and ferric ions as factors in the oxidation of pyrite has long been recognized.⁷ Astronomical increases in oxidation of pyrite by iron bacteria have also been observed.⁷ In general, the rate-determining step, oxidation of ferrous ion to ferric ion, occurs more rapidly at higher pH.⁷ Thus, pH does not appear to be a factor. Silica and clays, on the other hand, can catalyze the reaction.⁷ All in all, it appears that removing the pyrite oxidation products from the vicinity of the pyrite and minimizing contact with contaminated water reduces the overall contamination by pyrite oxidation.

Data for pH and iron concentration levels in a leachate when the water flow is periodically interrupted and air is blown through the waste are shown in Figure 3. The first parts of the curves (until the interruption for air) are like those in the continuous leach experiments (Figure 2). After air is blown through the column for 1 day, however, the pH drops upon resumption of leaching and the iron concentration doubles (285 ppm rises to 550 ppm). As the leaching continues, these parameters return to approximately the same values as those expected if no interruption had occurred. When air is blown through the column for 7 days, the drop in pH becomes much more pronounced, and the iron concentration increases 12-fold (78 ppm rises to 1000 ppm).

Too little data are available for a solid explanation about the behavior of the discontinuous leaching system. Two plausible explanations for the increases in acid and iron concentration, however, are increased oxygen transport and mini-static/equilibrium leaching sites. Since the waste never became dry during either air-flow period, small "ponds" of contaminated leachate could have formed. Unlike the flowing water with its relatively fixed amount of oxygen, these little "ponds" could easily supply their oxygen content to the reaction site and readily be replenished by the passing air.

The discontinuous leaching of coal waste indicates serious potential problems that might occur during the disposal of coal waste. Waste materials are generally discarded wet or damp. This should be a condition highly suitable for pyrite oxidation. Also wastes discarded in the midwest and east receive substantial amounts of rain before they are covered. These generally drain but remain damp for long periods. Again oxidation should be prevalent. Good disposal procedures may need to include considerations dealing with moisture content, spreading area, and time delay before covering in order to minimize acid and leachable iron production.

..... This is your last typewritten line

Please type to be deleted

and

do not type in this area

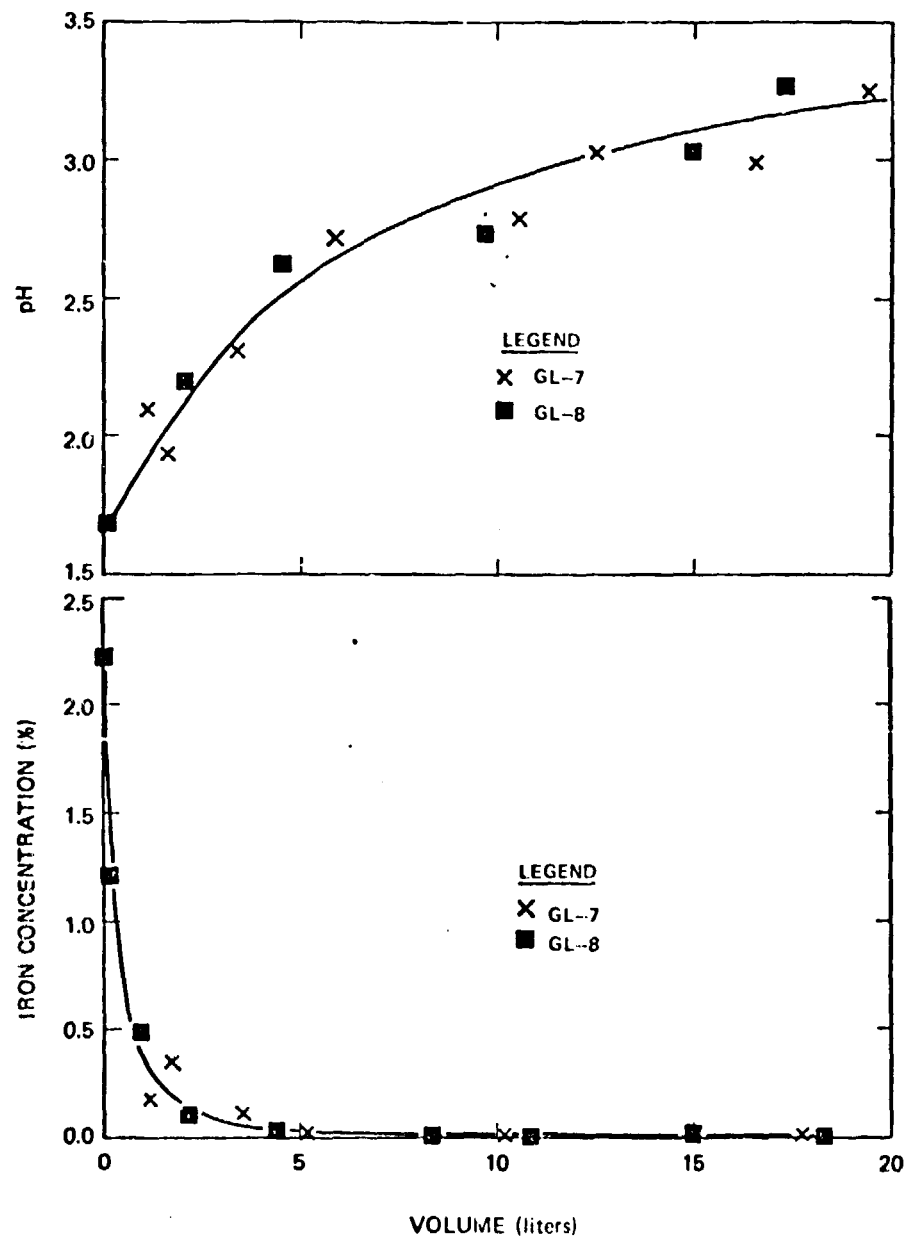


Figure 2. pH and Iron Concentration Changes as Water Passes Continuously through an Illinois-Basin Coal Waste.

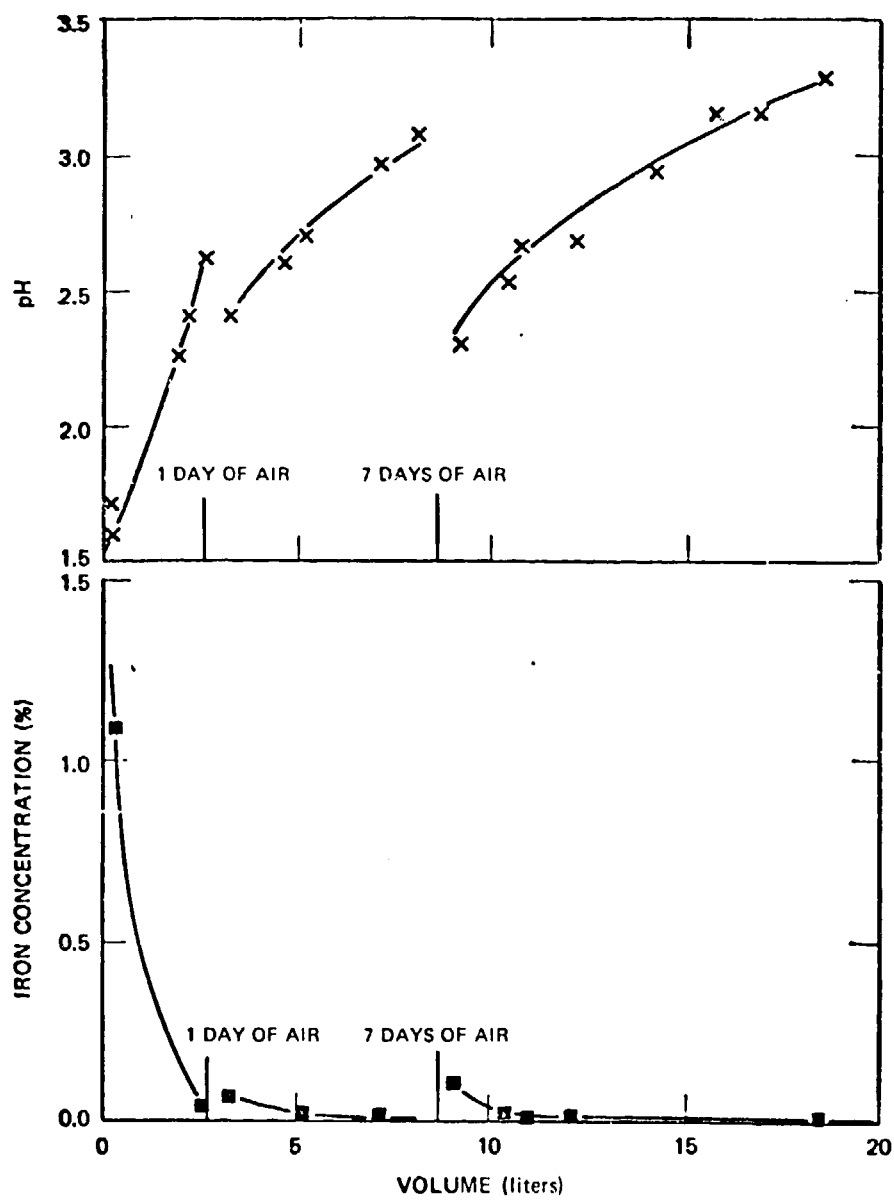


Figure 3. pH and Iron Concentration Changes as Water Passes Discontinuously through an Illinois-Basin Coal Waste.

Coal preparation waste contains a multitude of leachable elements. Data for 18 elements are presented here. Generally these elements occur in the waste leachates at levels related to their occurrence in the waste. Closer inspection reveals, however, that some elements are much more leachable than others. Thus, for Illinois-Basin waste iron is found to be present in waste leachate in high amounts, but this amount represents only a small percentage of the total iron in the waste. Cobalt and nickel, on the other hand, are not very plentiful in the waste, but are highly leachable. Aluminum, a major constituent of clays in the waste, is very poorly leached.

Oxygen availability is a prime factor in the production of soluble iron which is readily flushed from the waste. Particle size is less important. Under damp conditions and with plenty of air, pyrite oxidizes rapidly. This latter situation poses a problem for the plant operator, as coal preparation wastes are discarded damp and remain so via rainstorms for long periods before they are covered.

REFERENCES

1. National Academy of Sciences, "Underground Disposal of Coal Mines Wastes," Report to the National Science Foundation, Washington, DC (1975).
2. Wewerka, E. M.; Williams, J. M.; Wanek, P. L; and Olsen, J. D., "Environmental Contamination from Trace Elements in Coal Preparation Wastes-A Literature Review and Assessment," EPA-600/7-76-007 (1976).
3. Massey, H. F. and Barnhisel, R. I., "Copper, Nickel, and Zinc Released from Acid Coal Mine Spoil Materials of Eastern Kentucky," Soil Sci. 113 (3), 207-12 (1972).
4. Lowry, G. L., "Some Physicochemical Properties of Weathering Coal Spoils and Their Influence on the Growth of Pine Seedlings." University Microfilms (Ann Arbor, MI), Order No. 61-4968; Dissertation Abstracts 22, 1774-5 (1961).
5. Martin, J. F., "Quality of Effluents from Coal Refuse Piles," Pap. Symp. Mine Prep. Plant Refuse Disposal, 1st, Louisville, KY, Oct. 22-4, 1974, pp. 26-37.
6. Ruch, R. R.; Gluskoter, H. J.; and Shimp, N. F., "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," EPA-650/2-74-054 (1974).
7. Singer, P.C.; and Stumm, W., "Acid Mine Drainage: Rate-Determining Step," Science, 167, 1121 (1970).

← Figures and figure captions within this space - 5 1/4 x 7" →

..... This is your last typewritten line.....

← Please type to borderline →

and

Do not type in this area